This document was prepared in conjunction with work accomplished under Contract No. AT(07-2)-1 with the U.S. Department of Energy.

#### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161

phone: (800) 553-6847 fax: (703) 605-6900

email: orders@ntis.fedworld.gov

online ordering: http://www.ntis.gov/help/index.asp

Available electronically at <a href="http://www.osti.gov/bridge">http://www.osti.gov/bridge</a>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062

phone: (865)576-8401 fax: (865)576-5728

email: reports@adonis.osti.gov

TECHNICAL DIVISION SAVANNAH RIVER LABORATORY

**DEST AVAILABLE COPY** 

RECORDS ADMINISTRATION

DPST-66-570

INC INDEX NO .: 78342

CC: C. W. J. Wende, - J. W. Croach, Wilmington

D. F. Babcock - W. B. DeLong

W. P. Overbeck - A. A. Johnson, SRL

TIS FILE C. H. Ice

G. Dessauer RECORD COPY

J. W. Morris E. J. Hennelly - W. R. Cornman

E. C. Nelson - J. M. Boswell

H. E. Hootman

C. P. Ross

R. T. Huntoon

W. R. McDonell

W. C. Mosley, Jr. - J. A. Donovan J. R. Keski - J. T. Livingston

TIS File

Vital Records File

October 27, 1966

MEMORANDUM

TO:

P. H. PERMAR

FROM:

P. K. SMITH

HIGH TEMPERATURE STABILITY OF THULIUM OXIDE AND ITS COMPATIBILITY WITH REFRACTORY METALS

## INTRODUCTION

This report presents a theoretical analysis of the vaporization behavior of Tm203 and its compatibility with potential fuel capsule materials. Thulium-170 is a possible substitute fuel for <sup>210</sup>Po in thermionic and Poodle applications. The properties and high-temperature behavior of thulia are being compiled for the Isotopic Data Sheets.

### SUMMARY

Thulia appears to be an ideal fuel form for thermionic operation. only thulium oxide, cubic Tm2O3, has a melting point approaching 2400°C. Vaporization occurs with constant composition according to the competing processes:

$$Tm_2O_3(s) = 2TmO(g) + 1/2 O_2(g)$$
 Reaction 1

and

$$Tm_2O_3(s) = 2Tm(g) + 3/2 O_2(g)$$
 Reaction 2

Reaction 2 predominates slightly to produce a total vapor pressure given by

$$log P_{total}(atm) = 7.36 - \frac{31730}{T} (T in °K).$$

The total vapor pressure calculated from this expression is probably accurate within a range of three decades at 2500°K. Values for  $\Delta H_{298°K}$  for vaporization according to these two reactions are 443 ± 40 kcal/mole and 568 ± 1 kcal/mole, respectively. The boiling point of  $Tm_2O_3$  is estimated to be 4340 ± 300°K. More precise measurement of the vapor pressure can be made in the Knudsen effusion apparatus currently being used at SRL to measure the vaporization rate of curium oxides.

 ${\rm Tm}_2{\rm O}_3$  should be compatible with refractory metals and alloys at high temperatures. Thulia should not react with W, Re, or Mo or their alloys even up to its estimated melting point of 2645°K. Appreciable reaction with Ta should only occur above 2000°K in an open capsule. Solid solution ranges for  ${\rm Tm}_2{\rm O}_3$  in these metals and vice versa should be small at high temperature. Eutectic melting of  ${\rm Tm}_2{\rm O}_3$  and refractory metals or alloy compositions should be near 2000°C.

The decay product of Tm is another rare earth, Yb, which will be present in solid solution with  ${\rm Tm_2O_3}$  and exhibit nearly identical properties.

#### DISCUSSION

Two severe limitations of <sup>210</sup>Po fuels for use at high temperature are the absence of sufficiently refractory fuel compounds and the extreme pyrophoricity of the fuels presently being considered. Thulium-170, a possible substitute isotope for <sup>210</sup>Po, has a nearly ideal fuel compound in Tm<sub>2</sub>0<sub>3</sub>. Thulia is extremely high melting, has a very low vapor pressure, and is compatible with refractory alloys at temperatures well over 1920°K, which is the emitter temperature for thermionic diodes. Thulia will not dissolve easily in sea water or react with air to enter life processes if it is exposed in a mission failure. The excellent high-temperature behavior of thulia and some of its properties are described below.

The four most important properties that must be known for design and safety analyses of thermionic heat sources are melting point, thermal conductivity, vapor pressure, and compatibility with refractory metal containers. The vaporization behavior and vapor pressure of  ${\rm Tm_2O_3}$  have not been determined, but they can be reliably estimated using thermodynamic data available for  ${\rm Tm_2O_3}$  and similar data for other rare earth oxides. Considerable information on the compatibility of  ${\rm Tm_2O_3}$  with refractory metals exists or can be inferred from analogous studies in other rare earth systems.

## Refractory Properties of Tm203

Cubic  $\mathrm{Tm}_2\mathrm{O}_3$  is the only oxide of thulium. It is a "line compound," having a very small range of solid solution at high temperature. Up to 2550°K no structural phase transformations of  $\mathrm{Tm}_2\mathrm{O}_3$  are known that might cause cracking or degradation of a fabricated fuel form.

There is some evidence for a transition from cubic to hexagonal symmetry (A-Type  $\text{RE}_2\text{O}_3$ ) at 2550°K. (1) Thulia is one of the most stable oxides known, with  $\Delta\text{H}_f^\circ$  at 298°K equal to -451.4 kcal/mole. (2) The melting point of  $\text{Tm}_2\text{O}_3$  has not been measured, but it is estimated to be 2645 ± 25°K by analogy with the melting temperature of related rare earth oxides. (1,3)

## Vaporization Behavior of Tm203

The vapor pressure of thulia must be known to evaluate fuel redistribution over long periods of time in thermal gradients and to determine the rate of fuel loss on containment failure because of temperature excursion on burial, shallow trajectory re-entry, or launch pad fire.

In order to measure or calculate vapor pressure, the chemical process by which thulia vaporizes must be established. Thulia must vaporize to a gas of the same composition as the solid (congruent vaporization) because no other stable oxide can be formed by preferential loss of oxygen or metal.

There are several processes to be considered by which  ${\rm Tm_2O_3}$  may vaporize without change in composition. The principal vaporization process is the congruent vaporization process that develops the highest total pressure at a particular temperature. Of these possible processes two that develop the highest pressures are vaporization to  ${\rm TmO}(g)$  and vaporization to the elements, according to Reactions 1 and 2.

$$Tm_2O_3(s) = 2TmO(g) + 1/2 O_2(g)$$
 Reaction 1  
 $Tm_2O_3(s) = 2Tm(g) + 3/2 O_2(g)$  Reaction 2

The magnitude of the pressures developed by these two processes was estimated by the thermiodynamic analysis in Appendix I. The equations developed for the total pressure as a function of temperature in the range 0 to 4340°K (boiling point of  $Tm_2O_3$ ) are:

$$\log P_{\text{T}}(\text{atm}) = 7.78 - \frac{35900}{\text{T}} \text{ for Reaction 1,}$$

and

$$\log P_{\rm T}({\rm atm}) = 7.36 - \frac{31730}{\rm T}$$
 for Reaction 2.

While the errors in  $P_{\rm T}$  are large (a range of three decades), the error difference in  $P_{\rm T}$  for the two processes is small since the estimation errors common to both calculations cancel.

Pressures calculated from these equations are compared at three temperatures in Table I. At each temperature the pressure developed by Reaction 2 is greater than that developed by Reaction 1. Consequently, Reaction 2 represents the predominant vaporization process.

TABLE I

VAPOR PRESSURE OF Tm<sub>2</sub>O<sub>3</sub> AT VARIOUS TEMPERATURES

_	Pressure, atm	
Temperature, °K	Reaction 1	Reaction 2
2000	$6.8 \times 10^{-11}$	3.2 x 10 <sup>-9</sup>
2500	2.6 x 10 <sup>-7</sup>	4.4 x 10 <sup>-6</sup>
3000	6.5 x 10 <sup>-5</sup>	$6.0 \times 10^{-4}$

Thus, the equation for the total pressure developed by Reaction 2 is the proper expression for the vapor pressure of  $\text{Tm}_2\text{O}_3(s)$  and it is accurate within a range of three decades in the pressure at 2500°K.

The data in Table I (and the corresponding equations) are shown graphically in Figure 1 as typical Clausius-Clapeyron plots. If Reactions 1 and 2 are written so that each produces one total mole of gas, as they are in Figure 1, then the entropy change for both reactions should be about the same. Under this condition, the predominant reaction (the one that requires the least free energy to make a mole of gas) will be the reaction with the smallest heat of vaporization. Figure 1 shows that Reaction 2 does predominate. While the vapor pressure developed by Reaction 2 is higher, the pressure for Reaction 1 approaches the pressure for Reaction 2 at very high temperature, because the heat of vaporization for Reaction 1 is larger. The standard heats of vaporization at 298°K per mole of Tm<sub>2</sub>O<sub>3</sub> calculated from the data in Appendix I are 443 ± 40 kcal/mole and 568 + 1 kcal/mole for Reactions 1 and 2, respectively.

These curves are applicable up to the boiling point of  $\text{Tm}_2\text{O}_3$ . The boiling point was estimated from the temperature at which the vapor pressure equals 1 atm to be  $4340^\circ\text{K} \pm 300$ , which agrees with measured boiling points of other  $\text{RE}_2\text{O}_3$  compounds near  $4200^\circ\text{K}$ . (3)

White, Walsh, Ames, and Goldstein determined the vaporization process for several rare earth oxides, using mass spectrometric techniques to identify the relative importance of  $\mathrm{MO}_2(\mathrm{g})$ ,  $\mathrm{MO}(\mathrm{g})$ , and  $\mathrm{M}(\mathrm{g})$ . They found that the lighter rare earth sesquioxides vaporize congruently principally by Reaction 1. As atomic number increases, Reaction 2 becomes more important. The contribution of  $\mathrm{MO}_2(\mathrm{g})$  to the vapor pressure is negligible.

Similar experiments on other  $\text{RE}_2\text{O}_3$  compounds by  $\text{Panish}^{(5)}$  supported these observations. Panish estimated from measurements of mass spectrometer ion currents that the partial pressure of Tm(g) over  $\text{Tm}_2\text{O}_3$  is about

 $10^{-6}$  atm at 2300°K and that  $P_{Tm}/P_{TmO}$  is between 10 and 20. These observations are in excellent agreement with the values of  $P_{Tm}$  at 2300°K of 3 x 10-7 atm and  $P_{Tm}/P_{TmO}$  of 13, calculated from Equations 2 and 4.

If the fuel capsule were to develop a leak and continue to operate at 2300°K or higher, the weight of Tm<sub>2</sub>O<sub>3</sub> fuel that might be lost from a fuel capsule over a long period of exposure would be small. The maximum loss can be calculated from the equation,

$$P_{T} = \frac{W}{at \ 44.3} \sqrt{\frac{T}{M}} ,$$

where W is the weight loss, a is the area of the leak, t is the time, and M is the average molecular weight of the gas.

For example, only about 5 mg of  ${\rm Tm}_2{\rm O}_3$  would be lost through a pinhole leak of  $10^{-4}$  cm² in six months at 2300°K. The error in the weight loss calculated from this equation is directly proportional to the error in  ${\rm P}_{\rm T}$ . If a more accurate estimate of the fuel loss than can be calculated from the expressions for  ${\rm P}_{\rm T}$  given in Equation 4 of the Appendix is needed, the vapor pressure must be measured. The Knudsen effusion apparatus, already operating in the Actinide Materials Facility to measure the vaporization rate of curium oxide, can be used to measure the vaporization rate and vapor pressure of  ${\rm Tm}_2{\rm O}_3$  easily to 10% and, with more care, to 3%. If interest in  $^{170}{\rm Tm}$  increases and more accurate vapor pressure data are needed, these measurements will be made.

## Compatibility of Tm203 With Refractory Metals

## Reduction by Refractory Metals

Thulia should be compatible with W, Mo, and Re and their alloys even above its melting temperature, and with Ta up to 2300°K. Thus, from a

materials viewpoint, thulia may be ideally suited for operation as a heat source for thermionic or Poodle devices. Simple reactions of these metals with  ${\rm Tm_2O_3}$  to form Tm liquid and refractory metal oxides cannot occur because of the very high stability of  ${\rm Tm_2O_3}$  compared to the stability of the refractory metal oxides.

Reduction reactions with Ta, Mo, or W to form binary alloys and refractory metal oxides probably will not occur because thulium does not form binary compounds or extensive solid solutions with any of these refractory metals. Moriarity and Baenziger (6) found no intermediate compounds between W, Mo, or Ta and Gd or Dy and limited mutual solubility. Daane and Spedding (7) report less than 0.2 wt % Mo is soluble in Ce or La at 1570°K and find no intermediate phases. Spedding and Daane (8,9) found that no Ta-Tm compounds exist and that Tm will dissolve 1.5 wt % Ta to raise the melting point of Tm by 135° to 1950°K.

The reaction of  $Tm_2O_3$  with Re to form  $TmRe_2$  is possible if  $TmRe_2$  is sufficiently stable. The existence of  $TmRe_2$  seems certain since Lundin<sup>(10)</sup> has found  $YRe_2$ , which melts at 2790°K. However, Foex and  $Traverse^{(1)}$  have melted  $Tm_2O_3$  on rhenium filaments in high temperature X-ray experiments with no visual reaction observed or unexpected changes in X-ray patterns.

## Eutectic Melting

Melting of the eutectic composition formed between  ${\rm Tm_2O_3}$  and the refractory metal container would increase surface contact to enhance diffusion and would lead to fuel redistribution. But the eutectic temperatures for  ${\rm Tm_2O_3}$  and pure refractory metals systems are expected to be well over

2250°K. For example, the eutectic temperature for  $Y_2O_3$ -W is about 2405°K, which is 285° less than the melting point of  $Y_2O_3$ . No eutectic melting was reported by Hoyt, Cummings, Zimmerman and Perrine<sup>(11)</sup> at 2270°K between W and  $Dy_2O_3$ ,  $Sm_2O_3$  or  $Eu_2O_3$  (with melting points of 2610, 2595, and 2320°K, respectively). Eutectic temperatures between refractory metal alloys and  $Tm_2O_3$  will be lower than for the corresponding systems,  $Tm_2O_3$ -pure metals, but are expected to be near 2300°K.

#### Formation of Ternary Compounds

Reactions of  ${\rm Tm_2O_3}$  with the refractory metals and alloys to form ternary compounds or extensive solid solutions probably do not occur. No ternary oxides are known to exist whose stoichiometry can be represented by a stoichiometric combination of  ${\rm Tm_2O_3}$  and refractory metal. Some ternary compounds do exist, e.g., tungstates, molybdates, and tantalates, but they are oxygen-rich compared to the system  ${\rm Tm_2O_3}$ -M.

Walsh, Goldstein and White  $^{(12)}$  found that  ${\rm La_2O_3}$  and  ${\rm Nd_2O_3}$  react appreciably with Ta crucibles above 2000°K to produce vapor pressures of LaO(g) or NdO(g) that are comparable to the vapor pressure observed at temperatures 200 to 300° higher in inert crucibles, according to the reaction  $3~{\rm RE_2O_3}$  + Ta =  $5{\rm REO(g)}$  + RETaO<sub>4</sub>. Similar behavior would occur between Ta and  ${\rm Tm_2O_3}$  in an open system. In a closed capsule with no temperature gradients, tantalum will not reduce  ${\rm Tm_2O_3}$  or form  ${\rm TmTaO_4}$  even above the melting point of  ${\rm Tm_2O_3}$ , since rapid achievement of the equilibrium pressure of  ${\rm TmO(g)}$  would prevent the reaction from continuing.

#### Vapor Transport Reactions

The formation of small amounts of refractory metal oxide gas by limited reaction between thulia and the container metal at high temperatures presents the possibility of vapor transport erosion of capsule metal in a temperature gradient. This mechanism for incompatibility has been evaluated for tantalum transport, since tantalum is the refractory metal most likely to show such an effect.

Temperature gradients in a capsule should not cause a tantalum capsule to be eroded from the inside even though TaO(g) is very stable and has a fairly high vapor pressure at temperatures over  $2000^{\circ}K$ . Possible transport processes involving TaO(g) are all endothermic and could transport Ta only to cold surfaces where it exists initially anyway. Compatibility failure because of vapor transport in a temperature gradient is even less probable for Mo, W and Re since their gaseous oxides are much less stable than TaO(g).

## Experimental Confirmation of Compatibility

The compatibility of Tm<sub>2</sub>O<sub>3</sub> and other rare earth sesquioxides with W, Mo, Re, Ta, and Nb has been demonstrated in several experiments. Thulia has been heated to 2550°K in experiments of the order of hours of exposure on W and Re filaments by Foex<sup>(1)</sup> and to 2270°K on W and Mo filaments at SRL by W. C. Mosley in high temperature X-ray diffraction experiments. No reaction was observed either visually or by unexpected changes in X-ray pattern. Grossman<sup>(13)</sup> has cycled yttrium sesquioxide in a tungsten crucible through the melting point and observed only small

solubility effects of W in  $Y_2O_3$  and vice versa. Several researchers (12,14) have used tungsten effusion cells to study the vaporization behavior of  $RE_2O_3$ , including  $Tm_2O_3$ , and found no reaction with tungsten. Hoyt, et al,(11) have studied the compatibility of  $Dy_2O_3$ ,  $Sm_2O_3$ , and  $Eu_2O_3$  with Mo, W, and Nb by heating powdered materials in vacuum for 2 hr at 2070-2270°K and subsequently examining the product metallographically; no signs of reaction were observed between any pair of oxide and metal.

A thulia wafer has been heated in a welded tantalum container at 2200°K for 24 hr at SRL by J. R. Keski with no reaction observed metallographically or by X-ray diffraction analysis. Reaction between Ta and  ${\rm Tm}_2{\rm O}_3$  was observed in 1 hr at 2170°K under conditions where  ${\rm TmO}(g)$  was removed by flowing helium.

### Influence of Yb Decay Product

Thulia has the unique property of forming a decay product, ytterbium, that is almost identical in refractory character, composition, and structure with its parent. The ytterbium will form a solid solution with  $\text{Tm}_2\text{O}_3$  as  $\text{Tm}_{2-x}\text{Yb}_x\text{O}_3$ , and the high temperature behavior, stability, and compatibility of this solid solution will be nearly identical to  $\text{Tm}_2\text{O}_3$ .

#### APPENDIX I

## THERMODYNAMIC ANALYSIS OF VAPORIZATION OF Tm203

#### Vaporization by Reaction 1

From the Third Law of thermodynamics and the equilibrium constant for Reaction 1, the standard free energy change at temperature is given by  $\Delta G_{\rm T}^{\circ} = \Delta H_{\rm T}^{\circ} - T\Delta S_{\rm T}^{\circ} = -RT \ln R = -RT \ln P_{\rm TmO}^2 P_{\rm O_2}^{1/2}.$ 

From the stoichiometry for Reaction 1, the partial pressures of the gases are related by  $P_{02}=1/4~P_{TmO}$ , which when substituted into the free energy expression above gives

$$\Delta H_{\rm T}^{\circ} - T\Delta S_{\rm T}^{\circ} = -RT \ln P_{\rm TmO}^{2} (1/4P_{\rm TmO})^{1/2} = -RT \ln 1/2 P_{\rm TmO}^{5/2}$$
.

The total pressure is related to the partial pressures by

$$P_{\text{Total}} = P_{\text{T}} = P_{\text{TmO}} + P_{\text{O}_2} = P_{\text{TmO}} + 1/4 P_{\text{TmO}} = 5/4 P_{\text{TmO}};$$

so that

$$\Delta H_{\rm T}^{\circ} - T\Delta S_{\rm T}^{\circ} = -RT \ln 1/2(4/5 P_{\rm T})^{5/2} = -RT \left[ \ln 1/2(4/5)^{5/2} + \ln P_{\rm T}^{5/2} \right].$$

Rearranging and solving for  $\log_{10} P_T$  produces Equation 1.

$$\log P_{T}(atm) = \frac{2}{(5)(4.576)T}(T\Delta S_{T}^{\circ} - \Delta H_{T}^{\circ} - 4.576T \log 0.3)$$
 Equation 1

The standard heat of vaporization ( $\Delta H_{T}^{\circ}$ ) and the standard entropy change ( $\Delta S_{T}^{\circ}$ ) for the vaporization at a particular temperature are evaluated from the following equations:

$$\Delta H_{\mathrm{T}}^{\circ} = \left[2 - D_{\circ}^{\circ}(\mathrm{TmO}) + \Delta H_{\circ}^{\circ}_{\mathrm{vap}}(\mathrm{Tm}) + 1/2 D_{\circ}^{\circ}(O_{2})\right] + 2 \left[\mathrm{TS}_{\mathrm{T}}^{\circ} + \mathrm{T}(\frac{\mathrm{F}_{\mathrm{T}}^{\circ} - \mathrm{H}_{\circ}^{\circ}}{\mathrm{T}})\right] \mathrm{TmO}$$

$$\Delta H_{\mathrm{f}}^{\circ}(\mathrm{TmO}(\mathrm{g})) \qquad (\mathrm{cont'd})$$

(cont'd)

$$+ 1/2(H_{T}^{\circ} - H_{\circ}^{\circ})_{0_{2}} - \Delta H_{f}^{\circ}_{298}(Tm_{2}O_{3}) - (H_{T}^{\circ} - H_{f}^{\circ}_{298})_{Tm_{2}O_{3}}$$

$$\Delta S_{T}^{\circ} = 2S_{T}^{\circ}(TmO) + 1/2 S_{T}^{\circ}(O_{2}) - S_{T}^{\circ}(Tm_{2}O_{3})$$

The significance of these terms and their calculated or estimated values at 2500°K are described below:

# ΔH° for Reaction 1

 $D_o^{\circ}(TmO) = standard dissociation energy at 0°K for the decomposition of TmO(g) into gaseous atoms = 122 ± 20 kcal/mole from Figure 2<sup>(4)</sup>$ 

 $\Delta H_{\text{ovap}}^{\circ}(\text{Tm}) = \text{standard heat of vaporization of thulium at 0°K}$ = 58.4 kcal/mole<sup>(13)</sup>

 $1/2D_{\circ}(O_2)$  = standard dissociation energy at 0°K of  $O_2(g)$  into gaseous atoms = 60.5 kcal/mole<sup>(15)</sup>

The standard heat of formation of TmO(g) at 298°K calculated from the above terms is assumed to be the same as that calculated at 0°K.

 $S_{T}^{\circ}(TmO) = entropy of TmO(g) at 2500°K = 76 ± 2 eu, estimated<sup>(4)</sup>$ 

 $\left(\frac{F_{T}^{\circ} - H_{o}^{\circ}}{T}\right)_{TmO}$  = free energy function to extrapolate energy of TmO(g) from 0 to 2500°K = 67 ± 2 eu, estimated<sup>(4)</sup>

 $(H_T^{\circ} - H_{\circ}^{\circ})_{02}$  = difference in heat content of  $0_2(g)$  between 0 and  $2500^{\circ}K = 11.0 \text{ kcal/mole}^{(15)}$ 

 $\Delta H_{1298}^{\circ}(Tm_2O_3) = standard heat of formation of <math>Tm_2O_3(s)$  at 298°K =-451.4 kcal/mole<sup>(2)</sup>

$$(H_T^{\circ} - H_{298}^{\circ})_{Tm_2O_3}$$
 = difference in heat content of  $Tm_2O_3(s)$  between 298 and 2500°K = 84.6 ± 15 kcal/mole, estimated from Figure 3<sup>(16)</sup>

The standard heat of vaporization calculated from the above data is  $\Delta H_{2500}^{\circ} = 411 \pm 75$  kcal/mole at 2500°K. The uncertainty is the combination of uncertainties in the component terms, which were liberally assigned.

$$\Delta S_{2500}^{\circ}$$
 for Reaction 1

$$S_{T}^{\circ}(TmO) = 76 \pm 2$$
 eu, estimated<sup>(4)</sup>

$$S_{T}^{\circ}(O_{2}) = \text{standard entropy of } O_{2}(g) \text{ at } 2500^{\circ}K = 66.3 \text{ eu}^{(15)}$$

$$S_{T}^{\circ}(Tm_{2}O_{3}) = \text{standard entropy of } Tm_{2}O_{3}(s) \text{ at } 2500^{\circ}K = 98 \pm 10$$

$$eu^{(4)}$$

The standard entropy change for the vaporization at 2500°K is  $\Delta S_{2500}^{\circ}$  = 89 ± 14 eu.

The final expression for total pressure as a function of temperature according to Reaction 1 is obtained by substituting  $\Delta H_{2500}^{\circ}$  and  $\Delta S_{2500}^{\circ}$  in Equation 1.

$$\log P_{T}(atm) = 7.78 - \frac{35900}{T}$$
 Equation 2

for temperatures between 0 and 4340°K (assuming  $\Delta C_P^\circ$  equals 0 over the temperature range). The uncertainty in  $P_T$  at 2500°K, arising from a combination of the uncertainty of estimation in  $\Delta H_{2500}^\circ$  and  $\Delta S_{2500}^\circ$  is over a range of four decades. The uncertainty in  $P_T$  changes with temperature, but the magnitude at 2500°K is typical of the quality of the data.

#### Vaporization by Reaction 2

The free energy relation for Reaction 2, corresponding to that derived above for Reaction 1, is  $\Delta F_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ = -RT/nP_{Tm}^2 P_{O_2}^{3/2}$ .

From the stoichiometry, the partial pressures are related by

$$P_{O_2} = 3/4 P_{Tm}$$
; and the total pressure is given by

$$P_{T} = P_{Tm} + P_{O_2} = P_{Tm} + 3/4P_{Tm} = 7/4P_{Tm}$$

Substitution into the free energy expression above produces

$$\Delta H_{\rm T}^{\circ} - T\Delta S_{\rm T}^{\circ} = -RT \left[ \ln(3/4)^{3/2} (4/7)^{7/2} + \ln P_{\rm T}^{7/2} \right]$$

Again, rearranging and solving for log  $P_{\eta \eta}$  produces Equation 3.

$$\log P_{\text{T}}(\text{atm}) = \frac{2}{(7)(4.576)\text{T}} (\text{T}\Delta S_{\text{T}}^{\circ} - \Delta H_{\text{T}}^{\circ} - 4.576 \text{ T log 0.0915})$$

Equation 3

The component terms to calculate  $\Delta H_T^o$  and  $\Delta S_T^o$  are given below. Most of the quantities were calculated or estimated for Equation 1 above.

$$\Delta H_{T}^{\circ} = 2\Delta H_{298}^{\circ} V_{ap}^{\circ} (Tm) + 2(H_{T}^{\circ} - H_{298}^{\circ})_{Tm(g)} + 3/2(H_{T}^{\circ} - H_{298}^{\circ})_{O_{2}}$$
$$- \Delta H_{f}^{\circ} 298 (Tm_{2}O_{3}) - (H_{T}^{\circ} - H_{298}^{\circ})_{Tm_{2}O_{3}}$$
$$\Delta S_{T}^{\circ} = 2S_{T}^{\circ} (Tm(g)) + 3/2S_{T}^{\circ} (O_{2}) - S_{T}^{\circ} (Tm_{2}O_{3})$$

## $\Delta H_{2500}^{\circ}$ for Reaction 2

 $(H_T^{\circ} - H_{298}^{\circ})_{Tm(g)} = difference in heat content for Tm(g) between 298 and 2500°K = 12.2 ± 1.0 kcal/mole from Figure 4<sup>(4)</sup>$ 

The standard heat of vaporization at 2500°K is  $\Delta H_{2500}^{\circ} = 524.5 \pm 17 \text{ kcal/mole.}$ 

 $\Delta S^{\circ}_{2500}$  for Reaction 2

 $S_T^{\circ}(Tm(g)) = standard entropy of Tm(g) at 2500°K = 56 ± 2 eu, estimated<sup>(4)</sup>$ 

The standard entropy of vaporization at 2500°K is  $\Delta S_{2500}^{\circ}$  = 113 ± 14 eu.

Equation 4 is the derived relation between  $P_T$  and T obtained by substituting  $\Delta H_{2500}^{\circ}$  and  $\Delta S_{2500}^{\circ}$  into Equation 3.

$$\log P_{T}(atm) = 7.36 - \frac{31730}{T}$$
 Equation 4

for all temperatures between 0 and 4340°K, again assuming  $\Delta C_p = 0$  at all temperatures. An uncertainty within a range of three decades in the total pressure arises from the uncertainty of estimation in  $\Delta H_{2500}^{\circ}$  and  $\Delta S_{2500}^{\circ}$  in Equation 4.

PKS:sm

#### REFERENCES

- 1. Mark Föex and Jean-Pierre Traverse. C. R. Acad. Sc. Paris 261, 2490 (1965).
- 2. E. J. Huber, Jr., E. L. Head, and C. E. Holley, Jr. <u>J. Phys. Chem.</u> 64, 379, (1960).
- 3. K. A. Gschneidner, Jr. Rare Earth Alloys, p 245, D. Van Nostrand Co., Inc., New York, N. Y. (1961).
- 4. D. White, P. N. Walsh, L. L. Ames, and H. W. Goldstein. "Thermodynamics of Vaporization of the Rare-Earth Oxides at Elevated Temperatures: Dissociation Energies of the Gaseous Monoxides,"

  Thermodynamics of Nuclear Materials, p 417, International Atomic Energy Agency, Vienna, 1962.
- 5. M. B. Panish. "Vaporization of Rare Earth Oxides." J. Chem. Phys. 34, 2196 (1961).
- 6. J. Moriarity and N. Baenziger, unpublished information quoted in C. E. Lundin, "Rare Earth Metal Phase Diagrams," paper given at the Rare Earth Symposium, Annual Meeting Am. Soc. Metals, Chicago, November, 1959.
- 7. A. H. Daane and F. H. Spedding, ISC-530 (1954); Decl. September, 1965.
- 8. F. H. Spedding and A. H. Daane, IST-15, November, 1959.
- 9. F. H. Spedding and A. H. Daane, ISC-1116, April, 1959.
- 10. C. E. Lundin, "Rare Earth Metal Phase Diagrams," paper given at the Rare Earth Symposium, Annual Meeting Am. Soc. Metals, Chicago. November, 1959.
- 11. E. W. Hoyt, W. V. Cummings, D. L. Zimmerman, and H. E. Perrine.
  "Rare Earth Oxides and Rare Earth Borates Corrosion, Compatibility, and Radiation Effects," GEAP-3909, April, 1962.
- 12. P. N. Walsh, H. W. Goldstein, D. White. <u>J. Am. Ceram. Soc</u>. <u>43</u>(5), 229 (1960).
- 13. L. N. Grossman, "High Temperature Thermal Analysis of Ceramic Systems," presented at the American Ceramic Society Meeting, Washington, D. C., May 11-15, 1966 (to be published in J. Am. Ceram. Soc.).

- 14. F. H. Spedding, R. J. Barton, and A. H. Daane. <u>J. Am. Chem. Soc.</u> <u>79</u>, 5160 (1957).
- D. R. Stull and G. C. Sinke. Thermodynamic Properties of the Elements, Advances in Chemistry Series No. 18, American Chemical Society, Washington, D. C., 1956.
- 16. D. Sh. Tsagareishvili and G. G. Gvelesiani. Russ. J. Inorgan. Chem. 10(2), 171-2 (1965).

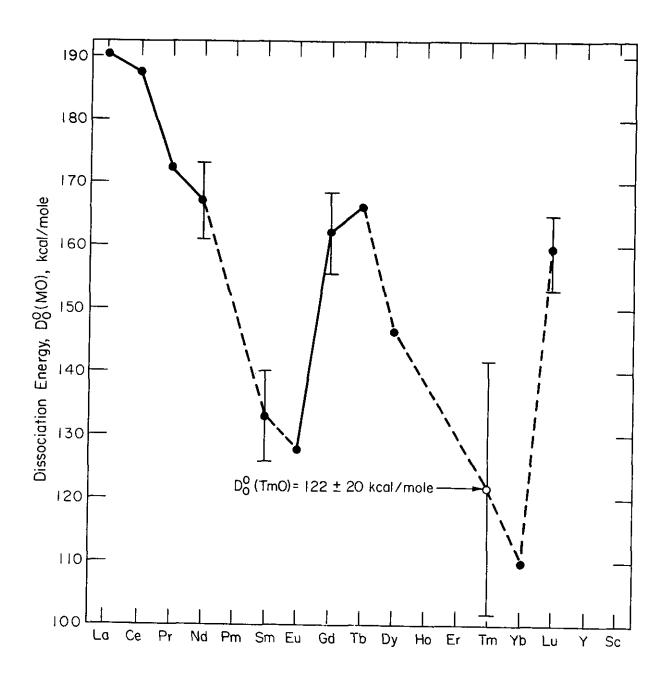


Figure 1. Total Pressure for Congruent Vaporization of Tm203

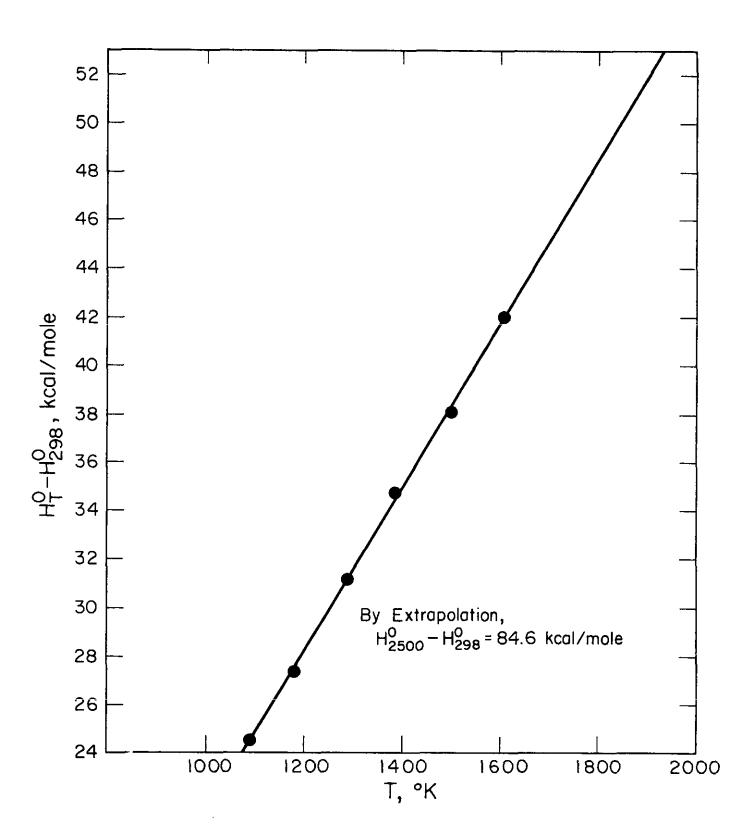


Figure 2. <u>Dissociation Energy for Rare Earth Monoxide Molecules</u> (4)

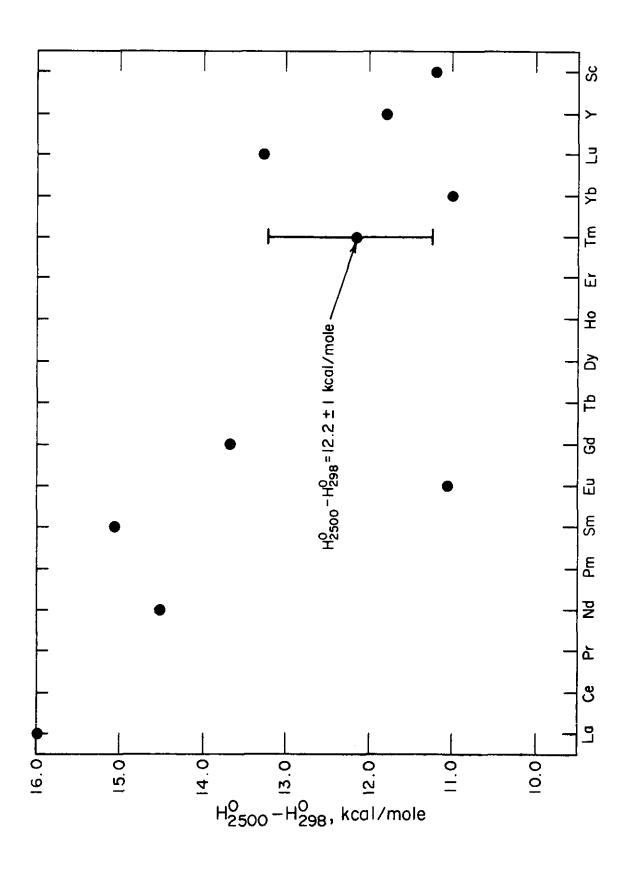


Figure 3. Change in Enthalpy of Tm<sub>2</sub>O<sub>3</sub> With Temperature (16)

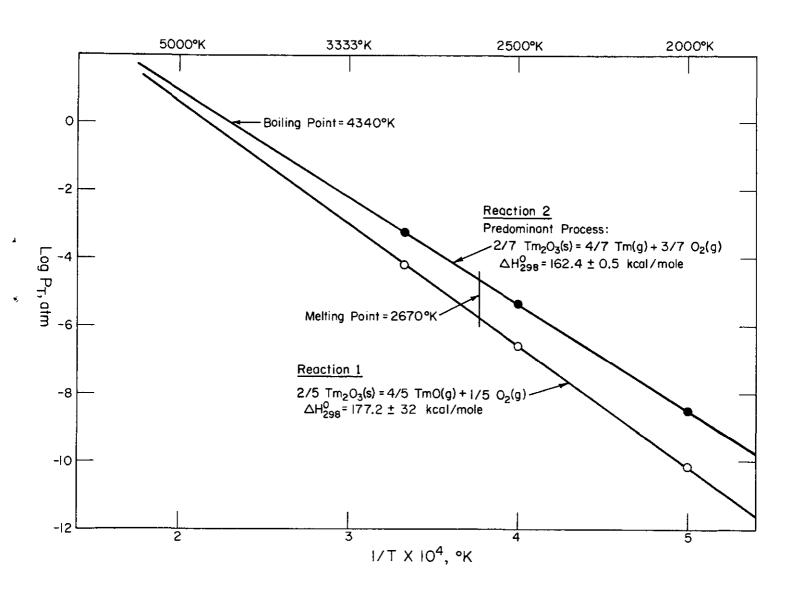


Figure 4. Enthalpy of Rare Earth Vapor at 2500°K.